Proceedings of the American Academy of Arts and Sciences.

Vol. XXXIII. No. 22. — June, 1898.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

ON THE CAUSE OF THE RETENTION AND RELEASE OF GASES OCCLUDED BY THE OXIDES OF METALS.

By Theodore W. Richards.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

ON THE CAUSE OF THE RETENTION AND RELEASE OF GASES OCCLUDED BY THE OXIDES OF METALS.

By Theodore William Richards.

Presented March 9, 1898.

In a recent critical discussion of Stas's work upon the atomic weight of carbon, Dr. Alexander Scott* of London had occasion to repeat some observations made at Harvard several years ago.† According to these observations, cupric oxide made from cupric nitrate had been found usually to contain several times its volume of occluded gases, chiefly nitrogen, and moreover it was shown that this gas resulted from the decomposition of minute traces of residual nitrate confined in the inmost recesses of the masses of oxide. Dr. Scott, however, could not find as much as one tenth of this amount of gas in his material. Since he was unable to explain the apparent discrepancy, it is one of the objects of the present paper to shed a clearer light upon the subject.

The essential point which escaped Dr. Scott's notice is this: the temperature of ignition is the most important condition determining the amount of the occluded gases. When the temperature is very high, nearly all of the imprisoned impurity is set free. To quote Dr. Scott's words, his oxide was exposed "for varying times to a full red heat in a muffle heated with gas." It is well known that at a temperature of about 1000° cupric oxide melts, with a very considerable loss of oxygen. It is obvious, then, that temperatures in this neighborhood are quite out of the question when the atomic weight of copper is concerned; hence, among the many experiments made by me in 1891, only three dealt with material which had been heated above 700°. The evidence of these three experiments (Nos. 59, 81, and 95), is unanimous in showing that

* Journ. Chem. Soc. Trans., LXXI. 559. (1897.)

† These Proceedings, XXVI. 281; Z. Anorg. Chem., I. 196.

most of the occluded impurity is set free at bright redness, and the first two of them agree quantitatively with the results of Dr. Scott.

Although it is thus evident that the English and American results are in no way inconsistent, I decided to repeat a part of the work, in order to obtain a more certain estimate of the various temperatures corresponding to the varying conditions of the cupric oxide. In my previous paper the higher degrees had been merely guessed, for they were not directly concerned in the point then under consideration.

The usual modes of determining high temperatures — the calorimeter, the air-thermometer, the bolometer, the meldometer, the platinum-iridium thermopile, etc. — are somewhat troublesome to use for a brief series of experiments of the present kind, so that it seemed best to determine the several temperatures approximately by finding for each temperature two substances, whose melting points were respectively above and below the point in question. For instance, an intensity of heat which would melt pure argentic bromide but not pure argentic chloride must be between 427° and 451°, a grade of accuracy more than sufficient for the present purpose. This method of determining the temperature has the great advantage of providing an approximate self-registering thermometer, occupying very small space and needing no connection with the outside air. The usefulness of the method obviously depends upon the number of substances easily obtained in a pure state, whose melting points are accurately known. For such knowledge of high melting points we depend mainly upon four researches, — those of Carnelley,* Le Chatelier,† Meyer, Riddle, and Lamb,‡ and Ramsay and Eumorfopoulos.§ Unfortunately the results of these four investigations do not always agree, their disagreement affording evidence of the great difficulty of measuring accurately high temperatures. At first sight the fact of the existence of such discrepancy might deter one from adopting this standard of reference, but further consideration leads to exactly the opposite conclusion. The melting points of pure salts must be an unchangeable standard, and the uncertainty of our knowledge regarding them must be largely due to experimental difficulties in the thermometric manipulation. These difficulties, if so serious in researches where everything was favorable to accuracy, must be largely augmented

* Carnelley, Journ. Chem. Soc., XXIX. 489, XXXIII. 273. (1876 and 1878.)

† Le Chatelier, Bull. Soc. Chem., XLVII. 300. (1887.)

‡ V. Meyer, Riddle, and Lamb, Berichte der Deutsch. chem. Gesell., XXVII. 3129. (1895.)

§ Ramsay and Eumorfopoulos, Phil. Mag., (5.), XLI. 360. (1896)

in a research like the present one, in which the temperature could not be made the sole issue of the experiment. Hence the melting point of a pure salt is the safest possible standard. The following table gives in parallel columns the salts chosen for the present scale of temperature, with the results of the four investigations, and the values of the melting points selected as the most probable.

TEMPERATURE SCALE.

	Carnelley Calorimeter.	Le Chatelier Thermopile.	Meyer Air Therm.	Ramsay Meldometer.	Value Selected.
Potassic nitrate	339	—	—	339	339
AgI, 2 AgBr, 2 AgCl	383	—	—	—	383
Argentic bromide	427	—	—	426	427
Argentic chloride	451	—	—	460	451
Plumbic chloride	498	—	—	447	498
Argentic iodide	527	—	—	556	527
Sodic biborate	561	—	—	—	561
Lithic chloride	598	—	—	491	598
Thallous sulphate	632	—	—	—	632
Strontic nitrate	645	—	—	570	645 (?)
Potassic bromide	699	—	722	733	720
Potassic chloride	734	740	800	762	760
Sodic chloride	772	775	815.4	792	790
Sodic carbonate	814	810	849	851	830
Strontic chloride	825	840	832	796	835 (?)
Sodic sulphate	861	867	863	884	865
Baric chloride	860	—	921	844	920 (?)
Potassic sulphate	—	1045	1078	1052	1060

The most serious discrepancies are to be noticed in the cases of potassic and sodic chlorides, where the respective averages have been chosen as the most probable values. These averages are almost identical with the figures obtained by Ramsay and Eumorfopoulos. On the other hand, Joly's meldometer, used by these investigators, seems to have been much less satisfactory at lower temperatures; for their melting points of plumbic chloride and lithic chloride are widely different from Carnelley's. Repeated qualitative experiments have convinced me that plumbic chloride is less easy to melt than argentic chloride, and lithic chloride less easy to melt than argentic iodide; therefore Carnelley's calorimetric results have been adopted here as the more accurate. Strontic nitrate, and strontic and baric chloride all begin to decompose in the air at or near their melting points; undoubtedly this fact is responsible for the very low results obtained by Ramsay and Eumorfopoulos in these cases. Obviously such salts cannot be relied upon as trustworthy thermometers, unless one takes the precautions observed by Meyer, Riddle, and Lamb in their work with the air thermometer. One is reminded of the interesting work of Hill upon changeable organic melting points.* The other substances in the list are sufficiently stable, and are easily obtained in a pure state. In the light of Le Chatelier's complete confirmation of Carnelley's results by means of the pyrometric thermopile, it is odd that the lamented Victor Meyer accorded Carnelley so little credit as he has done.

It is needless to state that pains was taken to eliminate impurities from these substances by recrystallization or other suitable means, and to dry the salts thoroughly, in the work which follows. If the temperature was below 800°, the dry coarsely powdered substances were contained in small melting-tubes of the hardest Jena glass, sealed while hot at both ends, and sometimes provided with a small platinum sinker to show whether or not the salt had liquefied. If, on the other hand, the height of the temperature excluded glass, the substances were contained in small cups beaten into stout strips of platinum foil. The small amount of impurity taken from the glass tubes in which some of the substances were melted could hardly have had much effect on the melting points until after a considerable mass of the substances had been melted; but then their mission had been fulfilled.

The table above might well be amplified to cover a wider range, as well as smaller differences of temperature, but such an amplification

* H. B. Hill, These Proceedings, XXIII. 219.

would constitute a research of some magnitude in itself. For present purposes the above will suffice.

Two forms of apparatus were used for determining the amount and the composition of the occluded gases. The first was identical in every respect with the most convenient of the three forms described in the original paper.* It consists of several bulbs blown in the bend of a glass tube bent at a right angle. One arm of the tube is temporarily closed by a stopcock, (not shown in the cut in the original paper, although mentioned in the letterpress,) and in this arm the gas, evolved in the bulbs by the solution of the cupric oxide in acid, is collected and measured over boiled water. When necessary the gas may be readily removed through the stopcock at the end of the arm; if a gas burette is attached here, of course the gas may be analyzed at once without further trouble.

For most of the experiments, however, Scott's modification of another of the original forms † was used. The mode of operating this apparatus was essentially similar to the method just described, although the bent tubes and bulbs are replaced by a small flask and funnel-tube. Scott's addition of a side tube to remove the displaced water distinctly increases the convenience and accuracy of the contrivance. For the details his paper should be consulted.

The two pieces of apparatus give identical results, which cannot be far from the truth. If at all in error the amount of gas collected must be too small rather than too large, for both oxygen and nitrogen are slightly soluble in water. This consideration was verified by fusing a specimen of oxide (another portion of which had been repeatedly analyzed in the usual fashion) with carefully prepared acid potassic sulphate in a Sprengel vacuum. The amount of gas evolved by this treatment was slightly greater, but only slightly greater than the amount obtained by the usual method, and its composition was essentially identical with that of the gas collected over boiled water. Since the question is one of relation, rather than of absolute values, the method involving the use of aqueous solutions was adopted because of its far greater ease of execution. Pains was taken to have the conditions of the solution of the oxide always as nearly as possible the same, so that the results should be strictly comparable with one another.

The first object of the present paper is to show more clearly the rela-

* These Proceedings, XXVI. 284. (1891.)

† These Proceedings, XXVI. 285, middle of page.

tion between the amount of gas retained by the oxide and the temperature used in its ignition. The material employed in these experiments was prepared by dissolving pure copper wire or electrolytic copper in pure nitric acid, and converting by heat the recrystallized cupricnitrate into basic nitrate and finally into oxide.* Platinum vessels were used throughout, whenever heating was necessary, excepting that one or two of the first ignitions were conducted in a porcelain boat. Three preparations of the oxide were made; one by the rapid decomposition of the nitrate, another by more gradual application of heat, and a third by the very slow action of a temperature just barely sufficient to effect the desired change. This temperature had been previously found by a special experiment to be about 275°, if the products of the decomposition remain in contact with the cupric oxide. The first of these preparations was the most coherent, and was capable of retaining the most gas; the second was less coherent and retained less gas, and the last was the most powdery and retained even less gas. Thus it is manifest that the physical condition of the solid is a factor in the question.

These specimens of the oxide of copper were subsequently ignited at varying temperatures for varying lengths of time in two different forms of furnace. For the first series a large tube or small muffle of Berlin porcelain capable of being heated to 1200° or more in a Fletcher furnace was used, but since it was found difficult to maintain the tube at a constant temperature throughout, this arrangement was later aban-

---

* It is interesting to note that the hydrate of cupric nitrate, which crystallizes from hot solutions, probably has the formula $3\,Cu(NO_3)_2 \cdot 8\,H_2O$ (analogous to cadmic sulphate), not $Cu(NO_3)_2 \cdot 3\,H_2O$ (Graham), as is usually supposed. Following are the analyses of three separate preparations, dried over moist potash (which does not dehydrate the crystals at ordinary temperatures) proving this point.

(1)	0.1739	gram of crystals	yielded	0.0471	gram of copper	=	27.08	per cent.
(2)	0.6310	" "	"	0.1705	" "	=	27.01	"
(3)	1.2897	" "	"	0.3448	" "	=	26.73	"
					Average	=	26.94	"

Theoretical value for $Cu(NO_3)_2 \cdot 3\,H_2O$ = 26.20 per cent of copper.
" " $3\,Cu(NO_3)_2 \cdot 8\,H_2O$ = 26.98 " "
" " $2\,Cu(NO_3)_2 \cdot 5\,H_2O$ = 27.35 " "

The crystals analyzed in No. 3 above were large and undoubtedly contained included mother liquor. Whether or not other hydrates exist, and what the transition temperatures may be, I did not take the trouble to discover. Much of our present data regarding water of crystallization has been rounded off in the manner indicated above. Undoubtedly many more such irregular ratios as 3 : 8 really exist than we are prepared at present to believe.

doned. All the subsequent ignitions were performed in a double crucible arranged in the manner shown in the diagram, the low platinum crucible or capsule used to contain the cupric oxide, being protected from radiation and convection by a number of superimposed crucible lids. The outer glazed porcelain crucible and the layers of asbestos board covering the draught holes united in excluding the products of combustion of the illuminating gas from the contents of the inner capsule. By means of this furnace, fed with a constant gas supply burning from a fourfold Bunsen burner, a surprisingly constant and uniform temperature may be maintained for an indefinite length of time.

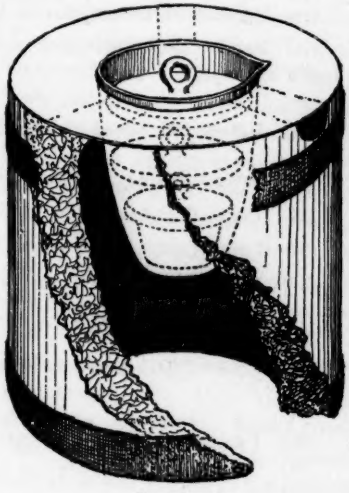

FIGURE 1.

In the following table are given the new series of results showing the relation of the total volume of gas retained to the temperature used in the ignition of the cupric oxide. The gas volumes are reduced to 0° and 760 mm. pressure, the reduction having been made by means of a Winkler-Lunge corrector arranged to give directly the exact volume of a mass of moist air which would measure a hundred cubic centimeters when dry and under standard conditions.

THE EFFECT OF TEMPERATURE ON THE TOTAL AMOUNT OF GAS OCCLUDED BY CUPRIC OXIDE.

First Series: First Preparation of Cupric Oxide.

(1)	1 gram CuO, heated 1 hour at 300° ±, * gave	0.18 c.c. gas.
(2)	" " " "	0.19 "
(3)	" " " "	0.21 "
	Average	0.19 c.c. gas.
(4)	1 gram CuO, heated 4 hours at 500° ±, † gave	0.69 c.c. gas.
(5)	" " " "	0.72 "
	Average	0.70 c.c. gas.

* Mercury thermometer.

† Plumbic chloride just fused; argentic iodide remained solid.

(6)	1 gram CuO, heated 1 hour at 830° ±, * gave	0.68 c.c. gas.
(7)	" " " "	0.69 "
(8)	" " " "	0.68 "
	Average	0.68 c.c. gas.
(9)	1 gram CuO, heated ½ hour at 870° ±, † gave	0.55 c.c. gas.
(10)	1 gram CuO, heated ½ hour at 900° ±, ‡ gave	0.08 "
(11)	1 gram CuO, heated ½ hour at 950° ±, § gave	0.05 c.c. gas.
(12)	" " " "	0.04 "
	Average	0.05 c.c. gas.
(13)	1 gram CuO, heated ½ hour at 1100° ±, ‖ gave	0.01 (?) c.c. gas.

Second Series: Second Preparation of Cupric Oxide.

(14)	1 gram CuO, heated 4 hours at 280° ±, ¶ gave	0.04 c.c. gas.
(15)	1 gram CuO, heated 1 hour at 290° ±, ¶ gave	0.12 c.c. gas.
(16)	1 gram CuO, heated 5 hours at 630°, ** gave	0.54 c.c. gas.
(17)	1 gram CuO, heated 3 hours at 830°, †† gave	0.57 c.c. gas.
(18)	" " " "	0.59 "
(19)	1 gram CuO, heated 5 hours at 830°, gave	0.57 "
	Average	0.58 c.c. gas.
(20)	1 gram CuO, heated 20 minutes at 870° ±, †† gave	0.42 c.c. gas.
(21)	" 150 " "	0.23 "
(22)	" " " "	0.14 "
(23)	1 gram CuO, heated 2 hours at 950° ±, †† gave	0.04 c.c. gas.
(24)	" " " "	0.07 "
(25)	" " " "	0.04 "
	Average	0.05 c.c. gas.

These two series of experiments, qualitatively and quantitatively similar to those carried out in 1891, lead to the following conclusions, which are copied verbatim from the paper on the atomic weight of copper: —

---

* Sodic chloride easily fused; strontic chloride just fused; sodic sulphate remained solid.

† Sodic sulphate just fused.

‡ Sodic sulphate easily fused; higher than last.

§ Baric chloride easily fused; potassic sulphate remained solid.

‖ Potassic sulphate fused, as well as the cupric oxide itself.

¶ Mercury thermometer.

** Thallous sulphate just melted.

†† See foot-notes to preceding series for criteria regarding temperatures 830°, 870°, and 950°.

"First, *that cupric oxide prepared by the ignition of the oxynitrate after Hampe's method contained between four and five times its volume of occluded gas.*

"Second, *that ignition of the oxide at very bright redness was capable of expelling a portion of this gas. The temperature required was nevertheless considerably above that which Hampe apparently employed.*"

The recent experiments add to these conclusions only greater definiteness. It is now clear that nearly all the gas is retained until a temperature of slightly over 860° is reached, when more than nine tenths of it is rapidly set free. Somewhat above this point the cupric oxide is itself partly decomposed; and in the neighborhood of 1000° the mixture of cupric and cuprous oxides fuses first into a mass resembling scoria, and then into a limpid fluid. It is evident that Scott must have used in his muffle a temperature somewhere between 850° and 1000°; for he found on the average 0.055 c. c. of gas per gram of cupric oxide, while my results obtained by means of temperatures in this neighborhood average 0.05 c. c. Moreover, some of his material was slightly reduced, but apparently none of it was melted.

It was clearly shown in the previous papers that the low results given by material ignited at temperatures below 450° are due to the presence of undecomposed cupric nitrate, which by its decomposition at higher temperatures yields the gas forming the subject of the present discussion.

The fact that prolonged ignition does not affect the amount of gas occluded may be inferred from the experiments just recorded; but in order to obtain more definite information on this influence of time, a third series of experiments was made.

The Effect of Time of Ignition on the Total Amount of Gas occluded by Cupric Oxide.

Temperature: The Fusing Point of Thallous Sulphate, about 640°.

(26)	1 gram of CuO, after ignition for 10 minutes, gave	0.56 c.c. gas.
(27)	" " "	0.57 "
(28)	" " "	0.53 "
	Average	0.55 c.c. gas.
(29)	1 gram of CuO, after ignition for 5 hours, gave	0.56 c.c. gas.
(30)	" " "	0.59 "
	Average	0.57 c.c. gas.
(31)	1 gram of CuO, after ignition for 20 hours, gave	0.56 c.c. gas.
(32)	" " "	0.59 "
	Average	0.57 c.c. gas.

A portion of the last specimen, which had been heated for twenty hours, was further ignited for five hours at about the fusing point of common salt (about 800°). Upon solution in acid this portion yielded the same amount, 0.59 c. c. of gas. Thus another of the conclusions arrived at in 1892 is confirmed: —

"Third, *that beyond a certain limit the time of ignition makes no important difference.*"

This is true, however, only below 850°. Experiments 20 to 22 show that when the imprisoned gas has once begun to be set free, at temperatures above 850°, the time is an essential factor; and that when sufficient time has been allowed, the expulsion of the gas is almost complete. Scott examined only cupric oxide from which he had thus expelled the gas.

In this connection it is interesting to note that Morse and Arbuckle * have recently verified, with apparatus far more elaborate and exact than ours, the results of Rogers and myself concerning the amount of gas occluded by the oxide of zinc.† Considering the fact that the manner of preparation of the substance undoubtedly affects the amount of gas retained, the closeness of the agreement is surprising. Only one of their conclusions is different from ours: in their opinion, there is no reason to believe that the temperature of ignition of the oxide has any effect on the composition of the occluded gas, while in our experiments the imprisoned oxygen decreased with increasing temperature. The basis of their reasoning is the supposition that the total amount of gas retained is dependent solely upon the temperature; using this total amount as a thermometer, they point out the fact that the smaller amounts of gas obtained in their experiments did not always contain the smaller amounts of oxygen; and hence they conclude that the temperature is not an essential determining cause of the composition of the mixture. In a letter answering some questions about the matter, Professor Morse kindly writes "We made every effort to secure constant temperatures for our oxide, giving the closest attention, to that end, to every detail of the firing of the furnace, the fuel, the location of the crucibles," etc. Since this is the case, and I cannot doubt the essential success of their efforts, it seems to me that their results have but little bearing upon the effect of *varying* temperatures on the oxide. The fact that their mixture of gases was by no means constant in composition is better explained by the supposition that some other cause besides the temperature influ-

* Amer. Chem. Journal, XX. 195. † These Proceedings, XXVIII. 200.

ences the relation of the volumes of oxygen and nitrogen retained, or else that the total amount of the enclosed gases is not a safe measure of the temperature. It will be shown that both of these inferences are correct, and hence that the logic of Morse and Arbuckle's point, correct in itself but unsafe in its premises, falls to the ground.

A careful study of all the data, Morse and Arbuckle's as well as ours, convinced me that, while the two gases must be evolved together, they behave subsequently in quite a different fashion. It is apparent immediately that the oxygen must escape at first much faster than the nitrogen, for the ratio of the two volumes in the nitric anhydride set free must be originally 5 : 2, while the average of Morse and Arbuckle's result showed that less than a fifth of the finally retained mixture consisted of oxygen. Part of the loss might be due to the preliminary formation of lower oxides, and to unequal diffusion, but this cannot account for so great a loss of oxygen. Even nitrous oxide should yield upon decomposition a mixture one third of the volume of which must consist of oxygen; and the fractional diffusion of this mechanically enclosed mixture should allow the lighter of its two constituents, nitrogen, to escape the more quickly of the two; hence the mixture should contain never less than thirty-three per cent of oxygen. The same anomaly is even more manifest in the case of cupric oxide, for from this substance nearly all the oxygen soon escapes even at comparatively low temperatures.

Why then does the oxygen escape the more easily of the two gases? This question introduces us at once to the second section of the paper, which deals with the composition of the occluded gases.

The first step toward answering the question is a certain determination of the facts, which have been doubted by Morse and Arbuckle. The three conditions which would be most likely to affect the amount and composition of the gaseous mixture are the temperature of ignition, the time of ignition, and the compactness of the solid material. In order to test the effect of these possible modifying causes experimentally, several series of analyses were made, both with zincic and with cupric oxide.

The zincic oxide was made by heating pure zincic nitrate for a long time at 280°. It was more compact than the cupric oxide, and undoubtedly contained residual traces of nitrate until further ignited.

The Effect of Temperature on the Total Volume of Gas occluded by Zincic Oxide.

First Series: Heated Three Hours.

(34)	1 gram of ZnO, after heating 3 hours at 660° ±, gave	0.365 c.c. gas.
(35)	" " " "	0.380 "
	Average	0.373 c c. gas.
(36)	1 gram of ZnO, after heating 3 hours at 750° ±, gave	0.233 c.c. gas.
(37)	" " " "	0.210 "
	Average	0.221 c.c. gas.
(38)	1 gram of ZnO, after heating 3 hours at 880° ±, gave	0.14 c.c. gas.
(39)	" " " "	0.18 "
	Average	0.16 c.c. gas.

Second Series: Heated Thirty Minutes.

(40)	1 gram of ZnO, after heating ½ hour at 750° ±, gave	0.366 c.c. gas.
(41)	" " " "	0.320 "
	Average	0.343 c.c. gas.
(42)	1 gram of ZnO, after heating ½ hour at 880° ±, gave	0.192 c.c. gas.
(43)	" " " "	0.192 "
	Average	0.192 c.c. gas.

Evidently, other conditions being equal, the total amount of gas retained decreases very considerably as the temperature of ignition is raised. Each one of these specimens of gas was analyzed, by means of Hempel's apparatus modified for use on a small scale,* with interesting results. The actual volume of *nitrogen* in every gram of material

Figure 2.

was found to be almost identical, diminishing only very slightly, if at all, as the temperature increased, and amounting to about 0.14 cubic centimeters. Thus the large differences in the total volumes are due almost wholly to *oxygen*, which varied from over sixty per cent in the first

* The most important modification was the arrangement for connecting pipette to burette. By blowing and drawing down the capillary it may be made to fit so perfectly into the fine rubber tube as to make the loss of small bubbles impossible. The diagram will make the idea clear. (Fig. 2.)

average, to less than twenty per cent in the third. The small amount of carbon dioxide present was absorbed almost completely by the boiled water over which the gases were collected; hence it need not be considered.* The actual volumes of nitrogen in the five averages were respectively 0.138, 0.133, 0.130, in the first series, and 0.152 and 0.127 in the second series; while the actual amounts of oxygen were respectively 0.235, 0.087, 0.030 in the first series, and 0.191 and 0.065 in the second. No better proof could be desired of the fact that zincic oxide allows its oxygen to depart more easily than its nitrogen. These results are wholly confirmatory of the results of Richards and Rogers already mentioned; but of course they do not explain how Morse and Arbuckle, working at nearly constant temperature, obtained inconstant results. To accomplish this explanation, the other possible causes affecting the retention of gases must be considered.

The Effect of Time of Ignition on the Amount of Gas retained by Zincic Oxide.

First Series: Just above the Melting Point of Thallous Sulphate.

(44)	1 gram of ZnO, heated at **660°** for 1 hour, gave	0.46 c.c. gas.
(34)	1 gram of ZnO, heated at **660°** for 3 hours, gave	0.36 c.c. gas.
(35)	" " "	0.38 "
	Average	0.37 c.c. gas.

Second Series: Just above the Melting Point of Potassic Chloride.

(45)	1 gram of ZnO, heated at **750°** for 10 minutes, gave	0.27 c.c. gas.
(46)	1 gram of ZnO, heated at **750°** for 20 minutes, gave	0.35 c.c. gas.
(40)	1 gram of ZnO, heated at **750°** for 30 minutes, gave	0.37 c.c. gas.
(41)	" " "	0.32 "
	Average	0.35 c.c. gas.
(47)	1 gram of ZnO, heated at **750°** for 60 minutes, gave	0.30 c.c. gas.
(48)	" " "	0.32 "
	Average	0.31 c.c. gas.
(36)	1 gram of ZnO, heated at **750°** for 180 minutes, gave	0.21 c.c. gas.
(37)	" " "	0.25 "
	Average	0.23 c.c. gas.

* These Proceedings, XXVIII. 205, 209. In a number of cases where pains was taken to measure the carbon dioxide, its volume never exceeded three or four per cent, and was usually about two per cent.

Third Series: Just above the Melting Point of Sodic Sulphate.

(49)	1 gram of ZnO, heated at 880° for 3 minutes, gave	0.49 c.c. gas.
(50)	1 gram of ZnO, heated at 880° for 5 minutes, gave	0.35 c.c. gas.
(51)	1 gram of ZnO, heated at 880° for 12 minutes, gave	0.29 c.c. gas.
(52)	" " "	0.25 "
	Average	0.27 c.c. gas.
(42)	1 gram of ZnO, heated at 880° for 30 minutes, gave	0.19 c.c. gas.
(43)	" " "	0.19 "
	Average	0.19 c.c. gas.
(38)	1 gram of ZnO, heated at 880° for 180 minutes, gave	0.14 c.c. gas.
(39)	" " "	0.18 "
	Average	0.16 c.c. gas.

In each of the series the same fact may be noted, — the fact that continued heating at any one temperature is capable of causing a slow evolution of gas from the oxide. Only in the second of these series is evident an initial increase in the amount of gas, indicating a maximum after less than twenty minutes of heating. This increase, which is manifestly due to the advancing decomposition of the traces of imprisoned nitrate, undoubtedly ceases after an hour's heating at 660°, or after three minutes' heating at 880°; hence it does not appear in the first and third series.

The steady loss of gas after this maximum has been attained — a loss increasing with time as well as with increasing temperature in the case of *zincic* oxide — is worthy of further attention, especially because it will be remembered that the amount of gas retained by *cupric* oxide remained almost constant until a very high temperature was reached. Analysis of the several specimens of gas showed at once wherein lay the explanation; for they showed as before that the maximal quantities of gas consisted chiefly of oxygen; while the gas obtained by the last two experiments consisted chiefly of nitrogen. Here again the nitrogen remained nearly constant, only diminishing from 0.20 c. c. at the maxima to about 0.13 c. c. at the minima; while the oxygen diminished in the same samples from 0.21 c. c. to 0.03 c. c.

It remains only, as far as zincic oxide is concerned, to show how wide a difference in the amount of gas may be caused by the original mode of preparation of the solid material.

THE EFFECT OF PHYSICAL CONDITION UPON THE TOTAL AMOUNT OF GAS RETAINED BY ZINCIC OXIDE.

(53)	1 gram of ZnO, prepared from zincic carbonate at **880°**, gave	0.00 c.c. gas.
(54)	" " " "	0.00 "
	Average	0.00 c.c. gas.
(55)	1 gram of ZnO, prepared from the nitrate at **280°**, not ignited, gave	0.01 c.c. gas.
(56)	A similar experiment gave	0.02 "
	Average	0.015 c.c. gas.
(57)	1 gram of ZnO, prepared from zincic nitrate, but heated to **880°** in a slightly reducing atmosphere, gave	0.05 c.c. gas.
(58)	A similar experiment gave	0.15 "
	Average	0.10 c.c. gas.
(42)	1 gram of ZnO, prepared by gentle heating of the nitrate at **280°**, and subsequent ignition for 30 minutes at **880°** in an oxidizing atmosphere	0.192 c.c. gas.
(43)	A similar experiment gave	0.192 "
	Average	0.192 c.c. gas.
(59)	1 gram of similar ZnO, prepared in the same way, but heated to **670°** for 3 hours and then preserved two weeks before heating ½ hour at **880°**, gave	0.292 c.c. gas.
(60)	A similar experiment gave	0.260 "
	Average	0.276 c.c. gas.
(61)	1 gram of more compact ZnO, prepared by heating the nitrate rapidly, and having been preserved for two weeks before being ignited for ½ hour at **880°**, gave	0.387 c.c. gas.
(62)	A similar experiment gave	0.396 "
	Average	0.392 c.c. gas.

The evidence of these results proves that the total amount of gas retained by zincic oxide varies with every detail of the method of preparation; hence this amount cannot serve as a sure guide to the temperature of ignition, unless a perfectly uniform sample is used for all trials.* Of course the amounts of nitrogen found in these samples varied widely; for the gas resulted from the decomposition of zincic nitrate, which was imprisoned in varying quantities according to the physical condition of the zincic oxide.

* Small quantities of such impurities as alkali and silica do not seem to affect the occlusion, however. See These Proceedings, XXVIII. 207.

Since so many circumstances regulate both the amount of gas and its composition, one is not surprised that Morse and Arbuckle obtained varying mixtures with eight different preparations of zincic oxide. It is true that their expulsion of the gases continued until it had become so slow that two successive weighings with intermediate heating gave constant weight; but the same causes of change must still have been at work, although far more slowly.

In the light of these interesting results, it seemed worth while to make a more elaborate investigation of the relation of the composition of the gases held by *cupric* oxide to the temperature used in its ignition. The material used in the following determinations was the soft powder made by the decomposition of cupric nitrate at 280°.

The Effect of Temperature of Ignition on the Composition of Gases retained by Cupric Oxide.

Time of Ignition, 1 *hour*.

(63) 0.32 c.c. gas from 1 gr. CuO heated at **520°** contained 18 per cent oxygen.
(64) 0.34 " " " " 15 " "
Average 15.5 per cent oxygen.

(65) 0.49 c.c. gas from 1 gr. CuO heated at **660°** contained 6 per cent oxygen.
(66) 0.48 " " " " 5 " "
Average 5.5 per cent oxygen.

(67) 0.47 c.c. gas from 1 gr. CuO heated at **750°** contained 3 per cent oxygen.
" " " " " 4 " "
Average 3.5 per cent oxygen.

0.05 c.c. gas from 1 gr. CuO heated at **1000°** ± contained 0 to 4 per cent oxygen, according to Alexander Scott.

It is evident that the cupric nitrate remaining in the cupric oxide had not been wholly decomposed by heating for an hour at 500° (experiments No. 63 and 64) and that we are dealing here with an increasing total, and a maximum similar in every respect to that already noted in the case of zinc,* except that in the present case more nitrogen is held, while the oxygen escapes at a much lower temperature.

---

* See page 412.

The Effect of Time on the Composition of the Gas retained by Cupric Oxide.

First Series: Temperature, 500°.

(Argentic Chloride easily melted; Plumbic Chloride scarcely melted.)

(68) 0.29 c.c. gas from 1 gr. CuO heated 2 hours contained 25 per cent oxygen
(69) 0.29 " " " " 23 " "
Average 24 per cent oxygen.

(70) 0.38 c.c. gas from 1 gr. CuO heated 8 hours contained 15 per cent oxygen.
(71) 0.42 " " " " 14 " "
Average 14.5 per cent oxygen.

(72) 0.46 c.c. gas from 1 gr. CuO heated 16 hours contained 8 per cent oxygen.

Second Series: Temperature, 520°.

(Just below the melting point of Argentic Iodide, but distinctly above that employed in the last series.)

(73) 0.15 c.c. gas from 1 gr. CuO heated for 15 min. contained 23 per cent oxygen.

(63) 0.32 c.c. gas from 1 gr. CuO heated for 1 hour contained 18 per cent oxygen.
(64) 0.34 " " " " 15 " "
Average 16.5 per cent oxygen.

(74) 0.48 c.c. gas from 1 gr. CuO heated for 2 hours contained 12 per cent oxygen.

(75) 0.49 c.c. gas from 1 gr. CuO heated for 16 hours contained 6 per cent oxygen.

Third Series: Temperature, 600°.

(Argentic Iodide fused easily; Lithic Chloride fused slowly.)

(76) 0.43 c.c. gas from 1 gr. CuO heated for 10 min. contained 12 per cent oxygen.
(77) 0.38 " " " " 12 " "
Average 12 per cent oxygen.

(78) 0.46 c.c. gas from 1 gr. CuO heated for 20 min. contained 13 per cent oxygen.

(79) 0.53 c.c. gas from 1 gr. CuO heated for 35 min. contained 10 per cent oxygen.
(80) 0.51 " " " " 8 " "
Average 9 per cent oxygen.

Fourth Series: Temperature, 640°.

(Thallous Sulphate just fused; Strontic Nitrate remained solid.)

(81) 0.21 c.c. gas from 1 gr. CuO heated for 2 min. contained 35 per cent oxygen.
(82) 0.19 " " " " 36 " "
Average 35.5 per cent oxygen.

(83) 0.43 c.c. gas from 1 gr. CuO heated for 10 min. contained 19 per cent oxygen.
(84) 0.45 " " " " 16 " "
Average 17.5 per cent oxygen.

(85) 0.46 c.c. gas from 1 gr. CuO heated for 8 hours contained 6 per cent oxygen.
(86) 0.45 " " " " 4 " "
Average 5 per cent oxygen.

It is clear that we are dealing here with a phenomenon precisely similar to that observed in the case of zinc. The decomposition of the remaining traces of nitric anhydride takes place much more slowly at low temperatures than at high ones, and the oxygen formed by this decomposition is liberated far more rapidly during the hotter ignitions.

A single series of experiments,* made some years ago with magnesic oxide, showed that this substance too acted in the same way, and it is probable that all the other oxides retaining traces of occluded gases would give similar results. The data obtained from magnesic oxide are repeated below, in order that all the facts may be at hand for the following consideration of the causes of the anomaly.

Gas Evolved from Magnesic Oxide.

(*Temperature of Ignition was about* 700°–800°.)

1 gram MgO	after ignition	30	minutes	gave 3.60	c.c. nitrogen and	7.2 c.c. oxygen.
1 gram MgO	"	60	"	4.72	"	6.3 "
1 gram MgO	"	75	"	4.84	"	4.4 "
1 gram MgO	"	135	"	5.44	"	3.6 "
1 gram MgO	"	195	"	5.24	"	2.8 "

Hypothetical Explanation.

The facts are now perfectly clear, and it remains only to account for them by means of a plausible theory. In the first place, there can be no question that the gases proceed from a residue of basic nitrate imprisoned in the oxides in question; the fact that oxides prepared from the carbonates contain little or no gas would alone be sufficient support for this point of view. The first matter to be considered is, then, the dissociation of this residual nitrate, which is probably wholly analogous to that of calcic carbonate as studied by Le Chatelier.† We may express this reaction, perhaps, in the following fashion, which indicates that the proceeding is supposed to take place in the gaseous phase, while the solids enter into the reaction solely by their vapor tension.

---

* These Proceedings, XXVIII. 209.

† Compt. Rend., CII. 1243 (1886). Nernst, Theoret. Chem., p. 377 (1894).

$$\underset{\text{Vapor.}}{Cu(NO_3)_2 . 3\ CuO} \rightleftarrows \underset{\text{Vapor.}}{4\ CuO} + [N_2O_5]$$

$$\downarrow\uparrow \qquad\qquad \downarrow\uparrow$$

$$\underset{\text{Solid.}}{Cu(NO_3)_2 . 3\ CuO} \qquad \underset{\text{Solid.}}{4\ CuO}$$

It is probable that Graham's basic cupric nitrate $Cu(NO_3)_2 . 3\ Cu(OH)_2$ is dehydrated before the nitric acid begins to leave; if it is not, of course three molecules of water must be added to the products above. The addition of the water does not affect the essential point in the following logic, however. The gaseous products of this reaction attain a pressure of 760 millimeters at about 280°.

The reaction represented above is evidently only a preliminary stage of the whole change; it may have scarcely begun, or may have run almost to an end in some cases before the dissociation of the nitric anhydride begins to enter into the problem. This dissociation may be complete, resulting in a mixture of the elementary gases, or it may (and does at ordinary pressures) stop at one of the lower oxides of nitrogen. Since the gases, whatever they may be, are necessarily held in microscopic cells, while their own volume under ordinary pressure is several times that of the total volume of the solid containing them, it is obvious that the pressure under which they exist must be very great. At this great pressure the stability of N_2O_5 must be very considerably increased, for the reaction $2\ N_2O_5 = 2\ N_2 + 5\ O_2$ is one which pressure must seriously affect because of the change of volume concerned in it; but more probably the peroxide of nitrogen may be the first product of the reaction. In any event, it is evident that the complete separation of the oxygen and nitrogen does not take place immediately, for much less nitrogen was yielded by the specimens of each oxide heated for a short time at comparatively low temperatures than by like specimens heated longer or hotter.

Both of these reactions, the decomposition of the cupric nitrate as well as that of the oxides of nitrogen, evidently then require time for their completion, so that the maximum of gas contents is not immediately attained. Besides being accelerated by heat they are also possibly both hastened by the escape of a portion of the oxygen, an interesting phenomenon which occurs side by side with the decomposition. To make the matter clearer, let us represent the dissociation of the oxide of nitrogen by the general formula

$$2\ NO_x = N_2 + xO_2.$$

The speed of this reaction is represented by the equation

$$-\frac{dc}{dt} = k c^2 - k^1 c_1 c_2^x,$$

an expression which increases in magnitude as c_2 (the concentration of the oxygen) diminishes. Since it is probable that k^1 is very small, — that the chief tendency of the reaction is from left to right, — this cause of acceleration is not an important one. In a similar way the decomposition of the oxides of nitrogen likewise accelerates the more complex reaction into which the solids enter.

In every case this decomposition of the oxides of nitrogen, and therefore that of the cupric nitrate, had nearly advanced to completion before the oxygen had all been expelled. This led to the existence of a maximum of gas volume after a brief heating, a maximum less marked in the case of cupric oxide than in the other cases because the extra oxygen escapes from cupric oxide almost as fast as it is formed. Thus many of the apparent eccentricities in the behavior of the gases find a simple and adequate explanation. The numerous results with different oxides were sought in the hope that the relations might be capable of quantitative proof according to the law of mass action, as well as of qualitative demonstration, but the great number of possible compounds and reactions made this hope vain.

It remains only to devise an hypothesis to explain perhaps the most interesting phenomenon under discussion, to show why the oxygen is capable of escaping more rapidly than the nitrogen. Obviously diffusion or transpiration cannot account for this; for any orifice, no matter how small, which would allow the oxygen to escape, must also allow the nitrogen to escape. The only possible explanation is the supposition that the oxygen finds its way out chemically, by uniting with metal or a lower oxide which has momentarily released some of its proper supply of oxygen. The displaced gas, being forced to find another berth, presently in its turn occupies the place of still another portion, and so on, until most or all of the excess has found its way out of prison. Of course the nitrogen cannot use this means of escape, for it is not surrounded by a compound which yields it upon dissociation; the nitrogen can only escape through holes originally present or formed by the rearrangement of the substance of the solid.

This hypothesis suggests Grotthus's obsolete explanation of electrolysis, or rather that of Clausius; for the most plausible conception is that in the hot rapidly vibrating solid a portion of the oxygen which

ought to be combined with the metal is always in a free state, and that this condition, by a recurring process of dissociation and association, permits relieving the high pressure of the oxygen in the cell. It is possible that water occluded in the oxide may play the part of a go-between, but there is no experimental evidence of this. It is no new idea to explain the diffusion of hydrogen through palladium, or of carbon through iron in the cementation process, and other similar phenomena, by a similar mechanical conception.

Quite in accord with this point of view are a number of facts. In the first place cupric oxide, the most easily reducible of the oxides investigated, parts with its occluded oxygen with the greatest ease, at the same time obstinately retaining the nitrogen. The progressive increase in the tendency to retain oxygen in the cases of zinc and magnesium corresponds to the increase in the difficulty of reducing these oxides. In other words, the least stable oxide is the one which has the feeblest hold upon the occluded oxygen. Cupric oxide begins to lose this impurity with great rapidity at 520°, zincic oxide loses it less rapidly even at 750°, and magnesic oxide is still more obstinate. It is probable, moreover, that in the cases of zinc and magnesium there is a slight amount of transpiration, for a small part of the nitrogen was found to leave at the higher temperatures. This transpiration ought to assist the oxygen also to escape, although in somewhat less measure than the nitrogen; but in spite of this possibility of more rapid escape, the oxygen is still held more firmly than in the case of cupric oxide. In this latter substance all the *nitrogen* is retained indefinitely at temperatures below 850°, forming the constant gas residue noted in the first experiments; only when the definite structure of the oxide is broken up, and the dissociation tension of the cupric oxide becomes so great that cuprous oxide begins to be formed, does the nitrogen take its flight. On the other hand a reducing atmosphere is needed to force zincic oxide to relinquish all its gas, unless an excessively high temperature is employed. Forty-three years ago Sainte-Claire Deville and Rivot showed that at a red heat such an equilibrium exists between zincic oxide, zinc, hydrogen, and water as to enable zinc oxide to be sublimed in a current of hydrogen, the dissociated oxide reforming when cooled.* This reaction undoubtedly enables the occluded gas to escape by destroying the structure of the solid when gases from the flame are present.

Again, the fact that many solids, the oxides in question among them,

* Ann. Chem. Phys., (3.), XLIII. 7, 477.

manifest upon heating the peculiar contraction called "sintering," is evidence of the existence of molecular instability and possibility of rearrangement. The hypothesis of partial dissociation at high temperatures is adequate to explain this.

It is obvious that, if the oxide is really dissociated, it should be capable of conducting electricity, because of the presence of traces of metal. In order to test this point, small platinum electrodes of 0.25 square centimeter in area and separated from one another by about 0.5 cm. were packed in pure specimens of the several oxides. Each porcelain crucible containing an oxide was gradually heated, after having placed the two electrodes in a circuit with a delicate amperemeter and four accumulators. When cold, the resistance of each of the oxides was at least 200,000 ohms. Upon heating, the cupric oxide began sensibly to conduct below a red heat, and at about 650° offered only about as much hindrance to the current as was afforded by 550 ohms, remaining constant at that point. On the other hand, zincic oxide fell in resistance only to about 15,000 ohms at 650°, and required fully 900° to bring it as low as 1,000 ohms; while the highest heat of the blast lamp could not cause the magnesic oxide to transmit as much as the twentieth of a milliampere, the least current capable of being observed upon the amperemeter. It is needless to say that any possibility of the presence of a reducing atmosphere was excluded, and the fact that each oxide returned almost if not quite to its non-conducting state after cooling is sufficient proof that the heat alone was the cause of the phemomena observed. These interesting results are fully in accord with the hypothesis that cupric oxide is slightly dissociated at a red heat, that zincic oxide is less dissociated, and that magnesic oxide, retaining its occluded oxygen with great obstinacy, is scarcely dissociated at all. Magnesic oxide, being one of the stablest of all compounds at high temperatures, could not be expected to show any appreciable dissociation or conductivity; and the wonder is, that the occluded gas is able to escape even as fast as it does.

This assumed partial thermal dissociation of solids must not be confounded with electrolytic dissociation (ionization); for the energy which determines the separation of the components in the present case is heat, and not electricity. The conductivity is not electrolytic conductivity, but only the metallic conductivity of the metal set free by a purely thermal dissociation. In order to prove this, a current of twenty milliamperes was transmitted through cupric oxide for three hours. This quantity of electricity would have carried nearly seventy milligrams of

copper from a cupric solution, aud since neither copper nor an oxide appeared adhering to the platinum negative electrode, it is safe to infer that the conductivity is not electrolytic. While these oxides thus conduct electricity without transferrence of material, it is undoubtedly true that many substances, even glass for example, which are non-conductors when cold, become capable of carrying a current *electrolytically* when heated. Melted salts are well known to be good electrolytic conductors, and Graetz* has found that this conductivity begins before the salts have melted. Our knowledge of the rationale of these facts is altogether too incomplete to afford satisfactory explanation of all the phenomena attending the passage of electricity through solids, liquids, or gases at high temperatures; and it is perhaps unsafe to record the conductivity of cupric oxide as a definite indication of the temporary presence of metallic copper in the case under discussion.

Following is a more certain proof that this dissociation is to be considered as analogous to the decomposition of limestone by heat. Here, as there, the gas, in the present case oxygen, must have a definite pressure of dissociation; but no appreciable amount of metal or lower oxide can form when the tension of the oxygen in the surrounding atmosphere is greater than this definite pressure. On the other hand, cupric oxide should lose not only its occluded oxygen, but all the oxygen that normally belongs to it, leaving metallic copper (or at least cuprous oxide), when heated in a perfect vacuum or in an inert atmosphere, if the hypothesis under consideration is tenable. This begins even in the air at about 1,000°. The search in chemical literature revealed a statement by Hilditch that cupric oxide ignited at lower temperatures in a vacuum weighs less than it did before, as well as one by Morley that the same substance slowly evolves a gas when heated in a vacuum.† Since it is hard to tell whether this evolution might not be merely that of the occluded gases, it was thought worth while to repeat the experiment.

Two grams of cupric oxide, which had been ignited for a long time in pure air until constant in weight, were found to evolve a gas steadily when heated in a vacuum to about the melting point of common salt (790°), provided that the gas was removed by a Sprengel pump as fast as it was formed. When allowed to attain equilibrium, this gas (which

---

* Wied. Ann., XL. 18 (1890).

† Hilditch, Chem. News, XLIX. 37 (1884). Morley, Am. J. Sci., XLI. 231 (1891).

repeated analysis showed to be almost pure oxygen containing only traces of nitrogen and carbon dioxide) was found to possess a tension of two or three tenths of a millimeter of mercury. A portion of the same material was heated for many hours more in a crucible to a full red heat; but upon subsequently heating it in a vacuum the evolution of gas proceeded just as before. Since all the occluded oxygen except two or three per cent had been expelled by the preliminary heating, this must have been structural oxygen. The conclusion was confirmed by the discovery of red cuprous oxide in the residue. Repetitions of the experiment showed that the tension of the gas increased enormously with the temperature, exceeding a millimeter before the glass became so soft as to collapse. In some of the experiments the best Bohemian glass was used, in others the hardest made in Jena. The nature of the glass seemed to be without influence on the result. The amount of gas evolved in a given time naturally depends upon the efficiency of the pump, as well as upon the temperature; in one of the experiments two cubic centimeters of oxygen were obtained in eight hours.

Ignition of the substance in an inert atmosphere should produce the same effect. Since cupric oxide is slightly dissociated by heat, perceptible amounts of oxygen should be removed by heating it in nitrogen, just as carbonic acid is removed from limestone by heating it in a current of air. This dissociation of cupric oxide must have its effect on any process involving the ignition of cupric oxide in a vacuum or in an inert gas. The determination of organic nitrogen by means of the Sprengel pump, for example, must be affected by it. The use of carbon dioxide as a displacing medium in the Dumas method probably disposes of the error, however; for carbon dioxide is itself dissociated by heat, and it undoubtedly furnishes enough oxygen to diminish greatly the decomposition of the cupric oxide.

In the light of these results, it is obviously advisable, when one desires to remove oxygen from a mixture of gases by means of hot copper, to maintain the last portion of the tube at a comparatively low temperature. Even then the issuing gas may not be absolutely free from oxygen.

Every one knows that auric oxide is excessively unstable, and that argentic oxide is completely decomposed even in an atmosphere of pure oxygen at comparatively low temperatures. The present results merely extend this behavior, in a much smaller degree, to cupric oxide, and the hypothesis carries the idea still further. The dissociation of zincic oxide must of course be yet less, while the tension of oxygen above magnesic

oxide even at high temperatures must be an infinitesimal far less in value than the tension of the gas in the vacuum needed for the production of X-rays.

According to the phase rule and the law of mass action these reactions must take place in the gaseous phase, — the only one present of variable composition. As an example, the case of copper is given below: —

$$\begin{array}{ccccc} 4\,CuO & \rightleftarrows & 2\,Cu_2O & + & O_2 \\ \text{Vapor.} & & \text{Vapor.} & & \text{Gas.} \\ \uparrow\downarrow & & \uparrow\downarrow & & \\ 4\,CuO & & 2\,Cu_2O & & \\ \text{Solid.} & & \text{Solid.} & & \end{array}$$

The occluded oxygen is supposed to escape by the oscillation, backward and forward, of this heterogeneous reaction. The ability of the system to be first dissociated and then associated in another place where more oxygen is present presupposes, however, great internal activity in the substance of the hot solids; and this internal activity is the most interesting conclusion to be drawn from the phenomena under discussion.

In short, no matter what point of view one adopts, or what mechanical picture one forms of the reaction, the necessity of ascribing the rapid escape of the oxygen to internal rearrangement seems to be inevitable.

Professor Morse, in another letter received since the foregoing was written, kindly tells me that, in the course of some admirable work upon the atomic weight of cadmium which he has just completed, he has had occasion to measure the gases occluded by cadmic oxide made from the nitrate. As one would expect, this oxide holds its occluded oxygen more firmly than copper, but less firmly than zinc. In fact, the behavior of the substance, according to Professor Morse's description, probably accords well with the hypothesis under consideration. His interesting results will soon be in print, and will speak for themselves. The fact that Rogers and I found no gas in our cadmic oxide in 1892 is easily accounted for by the circumstance that we used a bright red heat in the ignition, the oxide parting with both gases by the disintegration of its original structure, as the oxide of copper did with Scott. Since cadmium is volatile at high temperatures, however, it was natural that its dissociated oxide should have a wider opportunity of rearrangement than in the case of copper; and hence the crystalline structure of the ignited oxide observed in 1892. Nickel, another metal whose

oxide was investigated by Rogers, probably occupies its expected place near cadmium, as far as its oxide's capacity to retain oxygen is concerned. In some recent experiments in this laboratory, Cushman succeeded in partially decomposing nickelous oxide in a stream of nitrogen below 1200°. All these considerations are concordant with the hypothesis devised to explain the escape of occluded oxygen for metallic oxides.

The only point regarding this occlusion of gases left unexplained is the fact that in the experiments of Morse and Arbuckle the total amount of gas was in every case nearly the same, although the proportion of oxygen and nitrogen varied. This is a very interesting circumstance. The experimenters ignited their oxide to constant weight, in other words, until two successive ignitions caused no appreciable change; but it does not follow from this that the evolution of gas had ceased, — one can only maintain that it had become so slow as to be inappreciable. Evidently, then, the question to be answered is, — Why has the oxygen more difficulty in escaping when a small amount of nitrogen is present than when a large amount is present? The reason of this eccentricity may be because those specimens which contain the most gas are naturally the most porous and loosely held together, although usually formed in larger individual aggregations; and the freer atomic and molecular motion allowed by the looser structure permits the oxygen to leave more rapidly. Hence in each case the sum of the oxygen and nitrogen amounted to about the same volume. This hypothesis within an hypothesis is rather too uncertain to deserve much emphasis, however.*

In the course of some of my old experiments on the impurities in cupric oxide, it became necessary to reduce the substance in a current of carbon monoxide. Referring to this work, Dr. A. Scott, in the paper already cited,† expresses surprise at the existence of an admixture of hydrogen in this gas. His experience agrees with that of Stas in finding only a small amount of such gaseous impurity in carbonic oxide obtained from oxalic acid, while my results indicated a

* In this connection it is a matter of interest to note that Ramsay (Phil. Mag., (5.), XXXVIII. 206 [1894]) has found that the presence of nitrogen in a palladium bulb seems to prevent to some extent the diffusion of hydrogen into it. This observation is not unlike Morse and Arbuckle's; but if as a matter of fact an indifferent gas can produce such an effect, our present notions concerning semipermeable septa demand some revision.

† *Loc. cit.*, p. 563.

large amount. Lord Rayleigh, in the course of his recent valuable work on the density of gases,* concludes that his carbonic oxide also was free from hydrogen or hydrocarbons; and indeed there is no reason why this result should not be easily attained if one uses pure materials. Lord Rayleigh explains the existence of hydrogen in my carbonic oxide by drawing attention to the fact that in my case the gas, dried only by calcic chloride, was passed over red hot platinum sponge.

This explanation is undoubtedly correct. Many experimenters have shown that the reaction $CO + H_2O = H_2 + CO_2$ is an easily reversible one at high temperatures,† and in the presence of a large excess of carbon monoxide, it is obvious that nearly all of the trace of aqueous vapor would be reduced. For my purpose at the time, the source of the hydrogen was of no importance; it was only necessary to know the exact amount of the impurity, and this was suitably determined. It is satisfactory to know the cause of the discrepancy, however, as well as to know that it is easier to prepare carbon monoxide almost free from hydrogen than seriously contaminated with it. More often than we suspect, perhaps, are our carelessly planned efforts at purification apt thus to introduce more impurity than they eliminate.

In a recent number of the Journal of the American Chemical Society, (March, 1898,) F. R. M. Hitchcock has published a preliminary paper upon the occlusion of various gases by the oxides of metals, having apparently overlooked the Harvard investigations. It is satisfactory to see the phenomenon widely recognized; for an appreciation of this serious cause of possible constant error will result in the publication of fewer erroneous determinations of atomic weights than have appeared in the past. One should also bear in mind the fact that nitric acid is not by any means the only substance which is liable to leave appreciable contamination in material from which it has been expelled by heat. The number of such occlusions is far greater than most analysts imagine; this fact is not realized because the minute residues are often so hard to detect.

The evidence of this paper proves that in reality no discrepancy exists between the results of Scott, and Morse and Arbuckle, and those obtained at Harvard. The apparent disagreements were caused

---

* Proc. Roy. Soc., LXII. 204 (1898).

† Bunsen, Liebig's Annalen, LXXXV. 137 (1853). Horstmann, Ibid., CXC. 228 (1878). Bötsch, Ibid., CCX. 207. And especially Hoitsema, Zeitschr. Phys. Chem., XXV. 688, as well as others.

by the fact that the later experimenters investigated parts only of the wide field outlined in 1892, the relation of the parts to the whole being partially unperceived. The paper also shows that the unequal escape of oxygen and nitrogen imprisoned in the oxides of metals is a phenomenon of great interest, capable of shedding light on the internal kinetics of solids.

CAMBRIDGE, May 1, 1898.